THE ANALYST.

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OBITUARY NOTICE.

DR. JOHN HALL GLADSTONE.

With great regret we have to chronicle the death of one of our honorary members, Dr. J. H. Gladstone, which occurred suddenly on October 9. He was born in 1827, and was consequently in his seventy-sixth year. He studied chemistry first at University College under Graham, afterwards at Giessen under Liebig. He graduated as Ph.D. in 1848, and was elected F.R.S. in 1853.

Dr. Gladstone was the first president of the Physical Society on its formation in 1874, and was president of the Chemical Society from 1877 to 1879. His first paper was published in 1845, and from that time onwards he devoted his constant attention to scientific research, maintaining for many years a laboratory, with assistants, at his own expense. He engaged himself largely with chemistry and optics, and the points of contact between these two sciences. Thus, he was a pioneer in a line of work that has been much developed in more recent times, and which has led to important results. Amongst his investigations may be mentioned that of the solar spectrum, and his determination of the optical constants of a very large number of bodies; to him we owe much of our knowledge on the refractive indices of the essential oils. For his optical and electrical researches, together with much other work, he was awarded the Davy Medal of the Royal Society a few years since. So lately as the present year two papers—one written by himself, the other in conjunction with Mr. W. Hibbert—were read at the meeting of the British Association held in Belfast.

Dr. Gladstone was for some time Lecturer on Chemistry at St. Thomas's Hospital, and afterwards Fullerian Professor of Chemistry at the Royal Institution. He was the author of several books, amongst these "The Biography of Michael Faraday" and "The Chemistry of Secondary Batteries."

Dr. Gladstone was also engaged for many years in various philanthropic movements. From 1873 to 1894 he was a member of the London School Board, acting as vice-chairman for three years.

His death terminates a long career of solid, useful work in many directions, always carried on with unostentatious modesty and urbanity. His genial and kindly presence will be greatly missed at the many scientific meetings where he was a well-known and constant attendant.

THE PROPOSED STANDARDIZATION OF METHODS OF CHEMICAL ANALYSIS.*

By Bertram Blount, F.I.C.

There has been evident of late years a tendency to apply the principle of standardization to matters and in directions differing considerably from those in which the advisability of erecting and enforcing a standard is generally conceded.

The commonest examples of standardization — namely, that of weights, of measures, and of money—have come into existence and are maintained by their manifest necessity. Various mechanical standards are so convenient as to have become practically necessities; for instance, standard gauges for wire and sheet have been used very freely, and standard screw threads have also been found desirable.

But, passing from these simpler cases where standardization is universally conceded to be convenient to a consideration of the advisability of extending this principle to more complex matters, we enter into a region of polemic; the advantages of an artificial uniformity are less clear, and the disadvantages become more easily discernible and are ultimately prominent. As an instance of this may be mentioned the proposal to standardize sections of structural metals, sizes of test-pieces for mechanical tests, and methods of applying such tests.

If the difficulty of accepting the principle of standardization is considerable in the matter of mechanical testing, it becomes still greater in the case of chemical analysis.

In mechanical testing, it is recognised that the values obtained for strength in tension and compression, for elongation of a ductile test-piece, for resistance to shock and the like, are appreciably influenced by the conditions of the test, and, in consequence, there is something to be said in favour of standard methods of applying the tests. But there is no such justification for the adoption of standard methods in chemical analysis where the object in view is the determination in a given material of a definite substance; in such a case all methods which are chemically sound must give the same results.

But notwithstanding these obvious facts, a desire has arisen in some quarters for the formulation of standard methods of chemical analysis, and for their gradual imposition on the community of chemists; steps have been taken to secure this end, and it is necessary to decide whether this movement is laudable or not, lest judgment should go by default.

The wish to establish standard methods of analysis is no new thing. A serious proposition in this sense was put before the Society of Chemical Industry by Professor Lunge in the year 1884. Discussions followed in which leading chemists, many of whom are still with us, took part, and in the face of an evident conflict of opinion it became necessary to appoint a committee to consider the whole question. I have not been able to find that any report by this committee was published,

* Abridged from a paper read before the British Association at their meeting in Belfast, 1902.

and from the situation to-day it is fairly certain that no definite decision was arrived at.

About the same time, now nearly twenty years ago, the Society of Public Analysts occupied themselves with a similar subject. The methods of water analysis were discussed, and recommendations for a standard process were formulated. A like course was adopted for the analysis of milk, and some years later for the detection of butter in margarine by the Reichert-Wollny process.

It will be observed that in all these cases the substances to be examined are natural products of indeterminate composition, and that the methods for their examination are of the nature of empirical tests rather than of analysis proper. Such tests are often of the highest importance and utility for practical purposes, and from their nature are best performed under standard conditions, but they must not be confused with actual chemical analysis, which is under no such obligation to rule.

At the meeting of the British Association held in Bath in 1888 a committee was appointed "to consider the best methods of establishing international standards for the analysis of iron and steel." The initiation of this investigation appears to have been due to Professor J. W. Langley, who undertook the preparation of the necessary samples. Other national committees were invited to join in the work, and after some years certain of those committees reported. At an early stage of the proceedings the British committee defined the object of the inquiry as the provision and preservation of specimens of iron and steel of a composition most carefully ascertained. These were intended to serve as standards whereby the accuracy of any given process or any given worker might be checked. It will be observed that there is here no word of a standard method of analysis; the members of the committee were to be free to use the method they thought proper, and the results alone were to be the standard. But the members of the American committee seem to have held a different object in view; they applied themselves to the examination of methods, and especially of those for the determination of carbon. It may be conjectured that their objective was the provision of a standard method, but this aim was not attained, and no subsequent attempt in the domain of steel analysis has met with greater success. It is interesting to note that whilst no standard method of steel analysis has been arrived at, the improvement in existing processes and the device of new methods have continued without pause or set-back, and that this branch of analytical work has been brought to a high state of efficiency.

But the idea, although not realized, was by no means dead. C. B. Dudley, of the Pennsylvania R.R., in 1893 discussed the causes of discrepancy between the results of different chemists, and advocated the use of standard methods for avoiding these discrepancies. Quite recently (in 1901) a committee of the New York section of the Society of Chemical Industry approached the same subject in the same spirit, and has reported in favour of a standard method of analysis for cement and cement materials. I had the honour in May last of reading a paper before this body, in which I ventured to criticise the method in detail, and to dissent from the acceptance of a standard method.

These criticisms and objections were very frankly and fairly received and discussed, and it may be hoped that the discussion will induce some of those who

were perhaps over ready to except standardization on its superficial merits to consider its real and weighty disadvantages, and to confine their activity to those branches of analytical work in which some form of standardization is admittedly useful.

The introduction of standard methods for the analysis of coal, sugar, fertilizers, and feeding-stuffs and for water analysis has also been advocated in recent years, chiefly in the United States, and some of the proposed methods have been officially adopted by various associations.

These instances will suffice to show that there is an increasing tendency to propose standardization of analytical methods, irrespective of the nature of the material to be analysed, and it remains to consider how this tendency has arisen and what effect it is likely to have if it continues to grow without opposition.

In the first place, it will be seen that there are in this matter two schools of thought sharply differentiated. On the one hand, we have chemists so impressed with the necessity of avoiding discrepancies that they are anxious to set up standard methods, stated in such detail that a faithful observance of the prescriptions by two workers cannot fail to secure identical results. And there are others less confident of the success of this system. This conflict of opinion arises in great measure from confusion of thought. There are many operations performed by the chemist which are from their nature arbitrary. To take an extreme case, it is evidently impossible to carry out the Maumené test for oils or to determine the flashing-point of petroleum, and to obtain concordant results without having recourse to a fixed procedure. In the examination of potable waters such arbitrary methods are in wide and general employment, and yield much useful information. Feeding-stuffs and manures afford a similar case. "Citrate-soluble phosphoric acid" is a meaningless term unless the conditions of its extraction are laid down. The fractional distillation of crude benzol and the return of its computed contents of benzene is another instance.

But this sort of codification, though useful and often necessary, has nothing to do with analysis. The object of the analyst is to determine with the best precision in his power the constituents of the substance which he is analysing. Sometimes he cannot do this, and is forced to have recourse to the determination of the properties of the substance; that is to say, he is compelled to apply to the material under examination various arbitrary tests. Standardization for these tests is legitimate enough; standardization of analysis implies that analysis is an arbitrary procedure not based on ultimate chemical facts. This view is too grotesque for discussion.

To turn to the much-debated question of discrepancies in analytical results, which is at the root of the whole matter.

In trade it is necessary frequently to appeal to the analyst, and if the results given by one analyst differ from those of another, examining what is believed to be the same sample, much delay and expense may be incurred. The trader is usually unaware of the great difficulty which exists in procuring identical samples, and he is almost certainly ignorant of the slow and laborious character of all analytical processes having claim to be exact. From the former cause he is disposed to ascribe all differences to errors of the analyst, and from the latter he is inclined to urge

greater rapidity of work than is compatible with accuracy. Sometimes from bad sampling or from hurried or unskilful work discordant or erroneous results may arise. Then the trader seeks a remedy, and believes that it may be found in a standard method of analysis. It need hardly be urged before this assembly that such a conclusion is fallacious. The same imperfection in sampling, the same hurried and unskilful work will lead to the same erroneous results; the only difference will be that each Chemikant—for he cannot be called a Chemiker—will be entitled to say that he had followed the prescription as faithfully as he was able.

It is not likely that chemists who practise as independent consultants will submit to dictation, even from a committee of their peers, as to the methods they are to employ. A member of this branch of the profession, asked to determine in some material a definite constituent, is either competent to choose a suitable method, and to execute it accurately, or he is not. If he is, a standard method is superfluous; if he is not, his early retirement is desirable, and will probably occur from the operation of natural causes. But there are some consultants who are more or less identified with particular branches of the chemical trade; they are constantly called upon to carry out analyses or assays for the buyers and sellers of ores, metals, minerals, salts and the like, and usually the results obtained by the buyer's and the seller's chemist are compared, and may be found to disagree. Now, here is a plausible case for the use of a standard method. It is argued that if the two chemists concerned were to use the same process the likelihood of their disagreement would be diminished. There is even a limited truth in this; the likelihood of disagreement would be diminished to some extent because both operators would be exposed to identical chances of error, instead of different chances. But the object of analysis is not to obtain a false concord by repeating a process, errors and all, with Chinese fidelity; it is to arrive at the truth as closely as knowledge and skill will allow, and one of the recognised methods of doing this is to vary the conditions of experiment. How misleading are mere concordances is sufficiently shown by some of the earlier determinations of atomic weight vitiated by a systematic error, exposed at once on radically changing the method. If the atomic weight of nitrogen had depended on the determination of the density of the residuum obtained by eudiometric analysis, a considerable error would have been admitted in a fundamental figure for a period of many years.

The need of the buyer's and seller's chemist for identical results will best be met by insuring that they are sufficiently well trained to refuse to employ a faulty method; their choice among several sound methods is obviously a matter of indifference. It is only when the assay is from its nature arbitrary, and is, in fact, a conventional test, that an identity of method is necessary.

A great part of the clamour for standardization arises from the discrepancies which often occur between the results of different works' chemists, and it appears that the "standard" methods which have from time to time been proposed in the United States have the works' chemist as their particular objective. These discrepancies are highly inconvenient, not only immediately to those concerned, but ultimately as tending to discredit the value of analytical control of manufacturing processes. When last in America I took some pains to ascertain the opinion of

chemists on this point, and found that those who advocated the adoption of standard methods, when confronted with the grave objections which can be urged against them, took refuge in the necessities of the works' chemist, maintaining that only by the provision for him of standard methods could uniformity and accuracy be attained.

It cannot be denied that this view is defensible, but it is defensible on one ground alone, and that hardly likely to commend itself to the works' chemist. His friends, in their anxiety to help him, infer that he is incompetent, and needs to be guarded and guided like a schoolboy. Now, as a matter of fact, although often overburdened with work and most inadequately paid, the works' chemist has done much to advance analytical chemistry, originating some methods and improving many others. It is neither just nor courteous to assert that he, above all others, is in need of direction and supervision from without, and that he is willing to barter his right of individual judgment, according to his training and experience, for a bundle of prescriptions.

It is, however, unfortunately true, that while there is nothing in the nature of things why the works' chemist should not be as highly trained and as capable of individual decision as his consulting colleague, yet it remains a fact that some works' chemists are not fully competent, and, conscious of their deficiency, might even welcome the promulgation of a standard method by which a given analytical process shall be carried out. Such cases are freely advanced by the advocates for standardization, and doubtless afford some show of argument in favour of the movement. But surely it is better and sounder to direct effort, not towards the provision of rules for half-trained chemists, but towards insuring that the chemists are fully trained. And here one is met by the money question. At present the average manufacturer is so little alive to the absolute necessity of obtaining proper scientific and technical aid in the conduct of his business that he will offer to the chemist a salary hardly in excess of the wages of a skilled mechanic. Is it to be wondered at that the man who is willing to accept such remuneration should not be fully trained, that his knowledge should be empirical, and that he should need the prop of a "standard" method scientifically on a par with a cookery recipe? If it is the desire of those who advocate the standardization of chemical methods to promote the multiplication of analytical machines turning out results of artificial uniformity, no better course could be adopted than the prescription in detail of processes which shall relieve their user from the troublesome process of thinking. I do not like to suppose that this is the object deliberately desired, but it is well at least to recognise that it is likely to be attained by the successful establishment of standard analytical methods.

There are other results to be expected of wider and more general importance. Let us suppose that standard methods had been prepared and published with the consent and under the direction of some body of chemists of sufficient standing to make their pronouncements authoritative. The position of all chemists who ventured to disagree with the findings of this central body would become very difficult. In all cases of dispute, in all legal proceedings, these dissentients would be placed at a disadvantage; on them would be thrown the onus of proving, usually before a non-technical tribunal, that the method they preferred was as good as that of the central committee. Now, it is as certain as anything not actually accom-

plished can be, that the standard method at its best would be a compromise between the different processes in use by the various specialists in that particular branch of work, and would have the usual quality of a compromise—namely, the preference of expediency for principle. Consequently, no independent worker basing his process on what he conceived to be the soundest principles could avoid a conflict with a method which from its origin is a hybrid product. If the dissentient were not able to convince the lay tribunal that his process was reliable, a grave injustice might be done to him; if, on the other hand, he did so succeed, the standard process would be discredited. A whole vista of trouble and dispute can be foreseen. The endeavour here made to trace to its logical outcome the effect of standardization is sufficient to show that such a scheme, even if it could be regarded as desirable, would lead to such complications as to render it impracticable.

But there are still further drawbacks of a kind yet more serious. If a standard process is adopted by a central authority, it will be regarded by many as final, and all incentive to original inquiry in that direction will be removed. Periodical revision by a standing committee will probably be carried out, but naturally on the lines of the existing process, and with the view of improving it in detail. The deviser of a method radically different from that which is official will be regarded as a sort of chemical heretic, and will receive the treatment usually accorded to the heterodox. Now, analytical research, although not the highest form of chemical investigation, is of great value both as a school of training and as a means of perfecting the chief instrument of the chemist, whose work, unless constantly controlled by its aid, would be little better than a maze of ingenious speculation. Anything calculated to discourage the criticism of existing analytical methods and the device of new ones is, therefore, much to be deprecated.

There is too good a case against the standardization of methods of chemical analysis to make elaboration of argument necessary or wealth of instance and illustration desirable. The plain facts constitute so crushing an indictment, and appeal so strongly to every thinking chemist who is jealous of the dignity of his chosen profession, that their statement without ornament or rhetoric must suffice for conviction. But as there is, nevertheless, a respectable body of opinion in the contrary sense, it may not be superfluous to register a formal pronouncement that standardization is undesirable except in cases where arbitrary methods of examination cannot be avoided.

To turn to the construction of a positive policy. The spirit which is dissatisfied with the present status of the analyst, that does not hesitate to indicate the causes of errors and discrepancies, and is eager to incur serious and voluntary labour in order to diminish the frequency of their occurrence, is so entirely admirable that if directed towards a better end than the construction of a cramping and ineffective code it could not fail to animate a larger and more liberal project with its own zeal. There are many branches of analysis (as distinct from arbitrary methods of chemical examination) in which there still exists some doubt whether certain of the recognised methods are actually as reliable as the users of them maintain. It would be outside the scope of this paper to put forward a list of these discussable methods; every practising chemist can provide illustrations from his daily work, and the specialists

in any well-defined branch of analytical work would, if they agreed in nothing else, be thoroughly in accord with the idea that revision of many accepted processes, after proper experimental inquiry, might be usefully undertaken. To realize this idea it seems to me that there might be formed standing committees of chemists interested in particular branches of analytical work; that those committees should meet as often as is practicable, in order that their members might confer; that each should draw up a programme of work to be carried out by selected members of the committee, the programme to be directed to the examination of existing methods of analysis, to the elimination of sources of error which might be discovered, and to the device of new and improved processes; that the results of the deliberation of these committees should be published periodically, in order that chemists at large might be informed of the progress made and warned against the errors discovered. All these inquiries would be of vast value to professional chemists, who would be in a position to judge how far the methods indicated might usefully be received and adopted.

It will be seen that the programme suggested differs radically from that to which I have ventured to take exception. The latter involves the pronouncement of a defined method for the determination of a given substance; the former is directed to the discovery of latent errors, and to the provision of processes free from these. In the one case a set of rules is imposed from without; in the other, advance and improvement will take place from within, unfettered by canon and unhampered by rule. I think it not too much to say that the whole spirit of science, which is instinct with the love of freedom and the defiance of mere authority, will be found favourable to the plan which I have put forward, and will unconditionally condemn any attempt to standardize methods of chemical analysis.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOODS AND DRUGS ANALYSIS.

The Composition of Sheep's Milk. Trillat and Forestier. (*Ann. de Chim. anal.*, 1902, vii., 321-323.)—The authors have made analyses of a large number of samples of French sheep's milk taken during the months of February, March, and April. The following results are given as typical:

	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Total solids dried at 100° C. ...	20·03	19·58	18·90	18·56
Fat	7·40	7·42	6·98	7·18
Lactose	5·32	5·35	5·53	5·26
Casein	6·18	5·87	5·54	5·12
Ash	1·021	0·394	0·961	1·018
Calcium oxide	0·247	0·256	0·250	0·238
Acidity	3·7	3·0	2·66	2·8

These figures are considerably higher than the mean of the results obtained by Chevalier and Henri, Doyère, Gorup-Besanez, and other authors, viz. : Total solids, 12·4 ; fat, 4·2 ; lactose, 4 ; casein, 3·7 ; and ash 0·7 per cent. C. A. M.

The Determination of Lecithin in Milk. F. Bordas and S. de Raczkowski. (*Ann. de Chim. anal.*, 1902, vii., 331-333.)—The authors consider that the most rational method is to determine the glycerophosphoric acid in the milk in the following manner: One hundred c.c. of the milk are shaken with a mixture of alcohol (95 per cent.), 100 c.c.; water, 100 c.c.; and acetic acid, 10 drops. The coagulum thus obtained is filtered off and extracted with three successive portions of 50 c.c. of hot absolute alcohol. The united extracts are evaporated, and the residue dried on the water-bath and taken up with a small quantity of a mixture of equal parts of alcohol and ether. The filtered solution is evaporated to expel the ether, the residue saponified with potassium or barium hydroxide, and the soap solution decomposed with very dilute nitric acid. After separation of the fatty acids the filtrate is evaporated to dryness, and the residue mixed with 10 c.c. of concentrated nitric acid, and oxidized on the hot-water bath by the gradual addition of pinches of powdered potassium permanganate. The precipitated manganese hydroxide is then dissolved by the addition of a few drops of sodium nitrite solution (1 : 10), the nitrous vapours expelled by boiling, and the phosphoric acid precipitated with ammonium molybdate, and finally determined in the form of magnesium pyrophosphate. The weight of pyrophosphate thus obtained, multiplied by the factor 1·5495, gives the amount of glycerophosphoric acid in 100 c.c. of the milk. C. A. M.

The Colouring Matter and Sugar of Apricots. A. Desmoulière. (*Ann. de Chim. anal.*, 1902, vii., 323, 324.)—Truchon and Martin-Claude (ANALYST, xxvi., 102) examined the expressed juice of various fruits, including apricots, but did not find dextrose or any colouring matter soluble in acid or ammoniacal amyl alcohol in any of them. In repeating part of this work the author examined four samples of apricots of different origin, and found dextrose in each. In the two cases in which quantitative determinations were made the following results were obtained :

Sugar.	Fruit not completely Ripe. Per Cent.	Ripe Fruit. Per Cent.
Saccharose	3·131	3·814
Invert sugar	2·383	2·299
Dextrose	0·771	0·353

The apricots, pounded in a mortar with water, yielded a liquid from which a yellow colouring matter could be extracted by either acid or alkaline amyl alcohol. On evaporating the extract a yellow residue was left, which, on the addition of a drop of sulphuric acid, became indigo blue, changing to brownish-violet. This reaction is identical with that given by carotin, the colouring matter of the carrot. The colouring matter of the apricot can be distinguished from coal-tar colours by the fact that it does not dye silk or wool. C. A. M.

On the Influence of Cane-Sugar and Dextrin in the Bees' Food upon the Composition of the Honey. Von Raumer. (*Zeit. anal. Chem.*, 1902, xli., 333-350.)—The author has made a series of feeding experiments, of which the following was the most complete. The bees were fed upon 2 litres of a mixture of 2,530 grammes of dextrin syrup and 1,000 grammes of cane-sugar dissolved in $4\frac{1}{3}$ litres of water. The whole of the honey was collected in two jars, the first of which contained 590 grammes and the second 1,734 grammes. On analysis the following results were obtained :

	Jar I.	Jar II.
	Per Cent.	Per Cent.
Total solids	80·8	80·17
Water	19·2	19·83
Ash	0·299	0·220
Acidity in c.c. N alkali	4·6 c.c.	4·4 c.c.
Sugar { direct	65·0	64·56
Sugar { after inversion	65·96	65·28
Cane-sugar	0·91	0·67
Dextrin after fermentation	10·10	10·98
Polarization of 10 per cent. solution in 200-millimetre tube at 25° C. { direct ...	+5·7	+6·03
Polarization of 10 per cent. solution in 200-millimetre tube at 25° C. { after inversion ...	+5·4	+5·75
Sum of dry substances	76·30	76·41

The comparative composition of the honey and of the syrup solution used was :

	Honey.	Syrup Solution.
	Grammes.	Grammes.
Total sugar	1519·94	804
Cane-sugar	16·97	456
Dextrin	249·98	532
Total carbohydrates	1769·92	1336

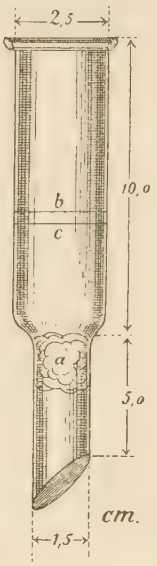
The author points out that it is remarkable that so little of the cane-sugar in the syrup remained uninverted, since in other feeding experiments on the same lines as much as 15 per cent. of cane-sugar was found in the honey. C. A. M.

Notes on the Sulphurous Acid of Beer. E. Jalowetz. (Reprint from *Mitth. Oesterr. Versuchsst. Brauerei und Malzerei*, Vienna, 1902, Heft x.; through *Chem. Zeit. Rep.*, 1902, 216.)—When sulphured and stored hops are boiled for an hour with wort in the usual manner, the amount of sulphurous acid in the latter does not increase. The sulphur of stored hops exists as sulphite. The use of sulphites in the brewery and the employment of sulphured malt increase the sulphurous acid of the beer. Freshly sulphured hops give up very little sulphurous

acid to boiling water. In laboratory experiments a rise in the amount of sulphurous acid occurs during the main fermentation of wort or sugar solutions, and a decrease during the secondary fermentation; but occasionally exceptions are to be found. In three breweries investigated by the author no appreciable increase in the sulphurous acid occurred during fermentation.

It should be noted that part of the sulphurous acid of beer is combined with aldehyde. The amount is small, but as the effect of the free acid is very different from that of aldehyde-sulphurous acid, when the total acid is determined attention must be paid to the quantity which is combined. F. H. L.

Identification of Bombay Mace. P. Schindler-Zwickau. (*Zeit. für offentl. Chemie*, 1902, viii., 288-290.)—To distinguish between Bombay and Banda mace the following test is recommended: About 5 grammes of the sample are placed in the tube shown in the illustration, the lower end of the tube containing the plug of cotton-wool *a*. On gently tapping the tube, the layer of mace will settle to the line *c*. The two lines *b* and *c* serve for gauging the quantity of mace in subsequent tests. Seven to 8 c.c. of 98 to 99 per cent. alcohol are added to the tube. This quantity is absorbed by the contents of the tube. Successive portions of 7 to 8 c.c. of alcohol are then added, and each as it runs through is collected in a separate test-tube. Should the sample consist of Banda mace, on adding a drop of lead acetate to the test-tubes the first extract gives a yellow or red precipitate, the second little, and the third remains clear, or nearly so. With Bombay mace, or mixtures of both maces, the first test-tube gives a more or less red precipitate, the colour increasing in intensity in the second and third tubes, and even showing after the twenty-fifth extraction. The alcohol used must not be weaker than 98 per cent. W. P. S.



The Refractometer Number for Cod-liver Oil. Utz. (*Zeit. für öffentl. Chem.*, 1902, viii. [16], 304-306.)—The refractometer values (Zeiss' instrument) of a number of samples of cod-liver oil are given. The results for Newfoundland oils lie between 80·8 and 81·5 at 15° C., and for Norwegian oils from 82·0 to 87·5. The adulteration of cod-liver oil with paraffin oil is easily detected by the refractometer, as the value for the latter is still lower than that of Newfoundland oils.

W. P. S.

Salicylic Acid as an Adulterant in Oil of Lavender. J. E. Weber. (*Chem. Zeit.*, 1902, xxvi., 875.)—The author has met with a specimen of oil of lavender, possessing excellent odour, which gave the following constants on analysis: Specific gravity at 15° C., 0·893; rotatory power, −6° 42′; acid value, 4·48; ester content reckoned as linalyl acetate, 35·52 per cent.; solubility, 2·5 volumes of 70 per cent.

alcohol. Apart from the acid number, which was a little high, no reason was given for assuming the oil not to be genuine; but on keeping for some time an unusual red colour developed. The colour disappeared on shaking the oil with alkali-metal hydroxide, a diminution in volume of 2·5 per cent. simultaneously taking place. It also disappeared on agitation with dilute hydrochloric acid, the aqueous extract containing iron. (This impurity was evidently derived from a bruise in the tin bottle holding the sample.) An alcoholic solution of the oil gave a dark-red colour with ferric chloride. Finally, by treating the material with potassium hydroxide, acidifying the liquid, extracting it with ether, purifying the product by repeated fractional precipitation as before, followed by crystallization from chloroform and water and decolorization with animal charcoal, white odourless crystals, melting at 156° to 157° C., were obtained, which proved to be salicylic acid. Direct tests by distillation under diminished pressure showed that no ester of salicylic acid was present. F. H. L.

Valuation of Ipecacuanha Root. G. Frerichs and N. de Fuentes Tapis. (*Arch. Pharm.*, 1902, ccxl., 401; through *Chem. Zeit. Rep.*, 1902, 254.)—Six grammes of the finely-powdered root are shaken in a dry flask with 60 c.c. of ether, 5 c.c. of ammonia are added, and after more agitation the vessel is set aside for one hour. Next 10 c.c. of water are run in, the whole is mixed up, and 50 c.c. of the ether are filtered off into a flask. Half the solvent is removed on the water-bath, and the residue is shaken out with 10 c.c. of decinormal hydrochloric acid in a separating funnel. The acid liquor is run through a paper, and the ether is washed twice with 10 c.c. of water; the combined aqueous portion is diluted to 100 c.c., and sufficient ether is added to form a layer 1 centimetre deep. Five drops of a 1 : 250 solution of iodeosin are then introduced, and the excess of free acid is titrated with decinormal potash. The volume of decinormal acid which has combined with the alkaloids, multiplied by 0·0241, gives the quantity of emetine and cephaeline in 5 grammes of the ipecacuanha root. F. H. L.

New Reaction for Quinine and Quinidine. E. Hirschsohn. (*Pharm. C. H.*, 1902, xliii., 367; through *Chem. Zeit. Rep.*, 1902, 201.)—If 10 c.c. of a neutral solution of quinine or quinidine, either as sulphate or hydrochloride, are heated to boiling with 1 drop of 2 per cent. hydrogen peroxide, a strong raspberry-red colour is produced, the intensity of which is proportionate to the amount of alkaloid present. The tint soon changes through blue-violet and blue to green. The reaction appears to be characteristic of the two alkaloids named. F. H. L.

TOXICOLOGICAL ANALYSIS.

The Guaiacum Test for Blood. D. Vitali. (*Giorn. di Farmac. di Trieste*, 1902, vii., 193; through *Chem. Zeit. Rep.*, 1902, 252.)—The author finds that guaiacum tincture is only coloured blue by hæmoglobin provided some turpentine oil is present, whereas all other substances which yield a similar colour oxidize the guaiacum of themselves, and do not require the turpentine. To render the test characteristic of blood, therefore, an aqueous solution of the suspected material is mixed with some fresh alcoholic tincture of guaiacum resin, and the whole is warmed to 40° or 50° C. If the mass turns blue some inorganic or animal oxidizing agent is present, and the test is not capable of showing blood; but if it remains colourless, and a blue appears on adding oil of turpentine, blood is undoubtedly to be found in the liquid examined. Ferrous sulphate behaves in the same manner as hæmoglobin, so that this salt must be absent before applying Van Deen's test. F. H. L.

ORGANIC ANALYSIS.

Estimation of Formaldehyde. A. Pfaff. (*Chem. Zeit.*, 1902, xxvi., 701.)—This process depends on the formation of a condensation product between formaldehyde and hydrazine, according to the equation:

$$2CH_2O + N_2H_4H_2O = C_2H_4N_2 + 3H_2O.$$

A solution of hydrazine hydrate, standardized with decinormal sulphuric acid, is added in excess to the liquid under examination, and after standing in a closed vessel for one hour, the excess of the reagent is determined by titration with the same acid, using methyl orange as indicator. The hydrazine hydrate solution does not keep its strength, but needs verification before each analysis. In standardizing it, it must be remembered that 1 molecule of sulphuric acid combines with 2 molecules of hydrazine, yielding the diammonium semisulphate $[N_2H_4]_2H_2SO_4$. The colour of the liquid obtained in this operation may be employed for comparison in the regular titration. The results quoted agree with those given by Romijn's iodine method.

F. H. L.

Estimation of Anthranilic Methyl Ester. A. Hesse and O. Zeitschel. (*Ber.*, 1902, xxxv., 2355; through *Chem. Zeit. Rep.*, 1902, 215.)—The authors consider that the process which Erdmann has proposed (ANALYST, 1902, xxvii., 125) for this purpose has one advantage over that which they themselves have recommended (*Ber.*, 1901, xxxiv., 296), inasmuch as it does not return the methyl ester of methylanthranilic acid or any other secondary or tertiary bases which may occasionally be present in the oil; but in all other respects their own method is preferable. Erdmann's process is not quantitative, while the action of the strong acids upon the oil renders it unfit for further examination. Perhaps, when methylanthranilic acid is expected, the bases may be isolated by means of Hesse and Zeitschel's process, and the product divided, titrating one half according to Erdmann, the other in their own fashion. F. H. L.

Determination of Oil in Linseed. A. Goetzl. (*Oesterr. Chem. Zeit.*, 1902, v., 413.) -The author has studied the comparative value of petroleum spirit and ethyl ether as solvents for the oil contained in linseed. The seeds were all finely powdered, dried for two hours at 95° C. in an atmosphere free from oxygen, and their albuminous constituents were coagulated with alcohol. The extraction of the seeds is more perfect with ethyl ether, but petroleum ether yields the purer product. All the foreign substances of the oils, such as cholesterin, etc., except "linoxyn," are more soluble in ethyl ether than in petroleum ether. The colouring matter of the seeds is taken up more readily by ethyl ether. Of the two liquids petroleum ether is easier to remove from the extracted oil. F. H. L.

Some Colour Reactions of Fatty Oils. H. Kreis. (*Chem. Zeit.*, 1902, xxvi., 897.)—When Bellier's test for sesamé oil (ANALYST, 1900, xxv., 50) is carried out as he described it, but with the resorcinol replaced by phloroglucinol, no colour is produced; if, however, either hot benzene or ether is used as the solvent, the red tint develops. The best reagent is a 1 : 1,000 solution of phloroglucinol in ether shaken with equal parts of 1·40 nitric acid and the sample under investigation. So examined, arachis, sesamé, cotton, walnut, peach-kernel, castor, and perhaps other oils, give strong raspberry-red colours in the non-aqueous portion of the test; while olive oil, lard, and butter remain colourless, or yield pale orange tints. If the process is modified by moistening 0·05 gramme of solid phloroglucinol with 3 to 5 drops of oil, and then adding an equal volume of nitric acid, sesamé behaves in a very characteristic manner—the acid becomes greenish-blue, the oil red; on introducing ether it becomes violet; and on shaking with water the ether turns red-brown, and the water is stained dark-blue. This water-soluble blue dyestuff is better obtained by shaking about 0·01 gramme of phloroglucinol with 2 c.c. of a 1 : 4 solution of sesamé oil in carbon tetrachloride, adding 1 c.c. of nitric acid as before and extracting with water. Resorcinol, with or without carbon tetrachloride, gives similar reactions with sesamé, but water and ether quickly decolorize the liquids.

The author has already shown that Bellier's reaction sometimes fails altogether, or appears but faintly, after prolonged agitation, when the oils are old; and he has also found that such oils, shaken with fresh sesamé and 1·19 hydrochloric acid, give the green noticed by Bishop in the case of old sesamé (*cf.* ANALYST, 1900, xxv., 49). This peculiarity has been observed with arachis, poppy, walnut, peach-kernel, cotton, and sesamé oils; and now it appears that in the same circumstances these oils refuse to give the reaction with phloroglucinol. Thus it happens that the failure of the Bellier test does not of itself prove the purity of a specimen of olive oil, and it is necessary to try such a sample with fresh sesamé oil and hydrochloric acid to insure the non-appearance of the Bishop green.

The author points out (*Chem. Zeit.*, 1902, xxvi., 932) that when an ethereal solution of phloroglucinol is used the solution at the end of the experiment should be diluted with water; otherwise a lively disengagement of nitric oxide may take place in a short time. F. H. L.

The Analysis of Commercial Lecithins. Imbert and Merle. (*Bull. de Pharm. Sud. Est.*, May, 1902; *Ann. de Chim. anal.*, 1902, vii., 350-351.)—The amount of phosphoric anhydride in lecithins varies from 8·75 to 9·45 per cent., according to the molecular weight of the lecithin. On boiling a lecithin with a mineral acid it is decomposed into phosphoric acid, a salt of choline, and free fatty acids, whilst alkalies convert it into alkali glycero-phosphate, choline, and alkali salts of the fatty acids. The authors' method is based upon these reactions, and also on the fact that mono-alkyl phosphoric acids are mono-basic with methyl orange, but dibasic with phenol-phthalein as indicator. If, then, after decomposition of the lecithin with an acid or an alkali, the liquid be exactly neutralized, with methyl orange as indicator, the amount of phosphoric anhydride can be calculated from the amount of alkali subsequently required to effect neutralization, with phenol-phthalein as indicator; since 2 molecules of alkali correspond with 1 molecule of phosphoric acid or 2 molecules of glycero-phosphoric acid.

In applying this method about 0·5 gramme of the sample is boiled for an hour with 50 c.c. of 5 per cent. sulphuric acid and then filtered, or 0·5 gramme is treated for thirty minutes with 50 c.c. of a 2 per cent. solution of potassium hydroxide. In each case the liquid is titrated with the two indicators as described above. The method is only applicable in the absence of phosphates soluble in water or in cold acids. Further information as to the quality of a lecithin can be obtained by determining the proportion of nitrogen it contains, as the ratio of phosphorus to nitrogen is approximately $\frac{31}{14} = 2{\cdot}21$, whatever the nature of the lecithin.

C. A. M.

New Reaction for Cholesterin. E. Hirschsohn. (*Pharm. C. H.*, 1902, xliii., 357; through *Chem. Zeit. Rep.*, 1902, 201.)—On heating with distilled trichloracetic acid, cholesterin dissolves with a fine red colour. The tint gradually deepens, becoming raspberry-red in fifteen minutes, blue-violet in twelve hours, and blue after twenty-four hours. One milligramme of cholesterin treated with 10 drops of trichloracetic acid and 1 drop of acetyl chloride gives an orange colour in half an hour, which darkens to a strong cherry-red in twenty-four hours, showing a greenish-yellow fluorescence.

F. H. L.

The Composition of "Kaki-Sibu." E. Pozzi-Escot. (*Ann. de Chim. anal.*, 1902, vii., 299, 300.)—*Kaki-sibu* is a commercial antiseptic product prepared from the juice of a plant, and widely employed in Japan for coating substances with a preservative surface. The sample examined by the author was a viscous reddish-brown liquid, with a strong odour of butyric acid. It was soluble in water, the solution giving a deep blue colour with ferric chloride, and becoming rapidly brown on the addition of an alkali. On exposure to the air the sample became coated with a firm pellicle, which was insoluble in water. When distributed over a textile fabric it formed a hard, very resistant coating. On analysis it gave the following results:

Specific gravity	1·025	
Total solids dried at 105° C.	5·82	per cent.
,, ,, ,, 115° C.	5·64	,,
Ash	0·345	,,
Tannin	3·59	,,
Volatile acid (as acetic acid)	0·234	,,
Fixed acid (as lactic acid)	0·115	,,
Nitrogen	0·00	,,

The tannin was not a glucoside. C. A. M.

Determination of Oxalic Acid in Urine. W. Autenrieth and H. Barth. (*Zeits. physiol. Chem.*, 1902, xxxv., 327 ; through *Chem. Zeit. Rep.*, 1902, 200.)—The entire quantity of urine voided in twenty-four hours is mixed with an excess of calcium chloride solution, ammonia is added to a strong alkaline reaction, the whole is well shaken and set aside for eighteen or twenty hours. The precipitate is collected on a paper, washed with a little cold water, drained well, transferred to a beaker, and dissolved in the minimum of hot hydrochloric acid (30 c.c. of 15 per cent. acid are usually sufficient). The resulting solution is extracted by successive agitation four or five times with 150 to 200 c.c. of ether containing 3 per cent. of alcohol. The extracts are brought into a large dry flask, and allowed to rest for one hour in order to separate the last portions of water, then passed through a dry filter. Next, 5 c.c. of water are introduced to prevent the formation of the diethyl ester of oxalic acid, and the ether is distilled off, shaking the aqueous residue, if necessary, with blood charcoal, and filtering it. The product is concentrated on the water-bath to 3 or 5 c.c., treated with calcium chloride solution and excess of ammonia, allowed to stand for a time, and then faintly acidified with acetic acid. The calcium oxalate is finally collected and washed, being estimated either by ignition into oxide or by titration, the former being preferable.

The authors' experiments show them that oxalic acid is a normal, and very probably a constant, constituent of human urine. F. H. L.

The Determination of Uric Acid in Urine. E. Richter. (*Zeit. anal. Chem.*, 1902, xli., 350-359.)—The author recommends the following method, devised by Jolles, as the most exact method of determining uric acid in urine. From 10 to 15 grammes of ammonium acetate are dissolved in 100 c.c. of the clear urine, which is then rendered faintly alkaline with ammonia, and allowed to stand for five to six hours. The precipitated uric acid is then collected on a filter, and washed with a 10 per cent. solution of ammonium carbonate until the filtrate is free from chlorine. The precipitate is then washed by means of hot water into a beaker, and boiled for about an hour with 0·1 gramme of magnesia to remove the excess of ammonium carbonate, after which 10 c.c. of sulphuric acid (specific gravity 1·4) are introduced, and the liquid oxidized by means of a 0·8 per cent. solution of potassium permanganate. This is first added to the boiling liquid 1 c.c. at a time until it is no longer rapidly decolorized, and then only 6 to 8 drops are added. When the separated

manganese peroxide no longer dissolves in the liquid when evaporated from about 500 c.c. to 100 c.c. (not less), there can be no doubt as to the whole of the uric acid having been oxidized to urea. The liquid is now evaporated to about 30 c.c., and any manganese peroxide dissolved by the addition of a few drops of $\frac{N}{10}$ oxalic acid, after which the beaker is immersed in cold water and continually agitated, whilst sodium hydroxide solution (32° Bé) is added 1 c.c. at a time until the reaction becomes alkaline to litmus. The liquid is then transferred to a Reichert's nitrometer, and shaken with 25 c.c. of a solution prepared by dissolving 80 grammes of sodium hydroxide in water, adding 25 grammes of bromine, and diluting the liquid to a litre. The amount of nitrogen liberated is corrected for temperature and pressure, and calculated into the corresponding amount of uric acid.

In this way the author obtained results ranging from 98·5 to 100·3 per cent. of the amount of uric acid used in test experiments. As a rule, the results given by this method were from 1 to 2·5 per cent. higher than those yielded by the Ludwig-Salkowski method, which, however, has been admitted by its authors to give results about 2 per cent. too low. C. A. M.

The Oxidation and Estimation of Uric Acid and Urates. J. F. Tocher. (*Pharm. Journ.*, 1902, 161-166.)—As urates are quantitatively converted into urea by boiling with dilute sulphuric acid and chromic anhydride, the uric and urea nitrogen can be determined in urine as follows: A measured volume of the urine is saturated with solid ammonium chloride, and the ammonium urate collected on a filter and washed with ammonium chloride solution. The urate is then dissolved in dilute soda solution, and boiled to drive off the ammonia; after acidifying with dilute sulphuric acid 2 to 3 grammes of chromic anhydride are added, and the solution is boiled. It is then cooled and transferred to a nitrometer, and the nitrogen liberated with hypobromite as usual. One c.c. of nitrogen is equivalent to 0·00375 gramme of uric acid. An alternative method is to boil 10 c.c. of the sample with about 2 c.c. of dilute sulphuric acid and 2 grammes of chromic anhydride for two minutes. The solution is then cooled and made up to 10 c.c.; 1 c.c. of this is measured into a hypobromite tube, and the liberated nitrogen read off. On separately estimating the urea in 1 c.c. of the urine, from which the urates have been precipitated as barium urate, and deducting the amount found from that obtained by the chromic anhydride treatment, the difference multiplied by 1·4 gives the uric acid. W. P. S.

A New Method of Organic Analysis. P. Thibault and A. C. Vournasos. (*Bull. Soc. Chim.*, 1902, xxvii., 895-901.)—It is stated that by means of the apparatus devised by the authors all the disadvantages of the ordinary method of combustion are obviated, and several analyses can be made in a day. It consists of a vertical steel tube, 20 centimetres in length and 5 centimetres in diameter, terminating below in a spherical bulb. On the side of the tube near the top is brazed a narrow steel tube, bent once at a right angle, and provided outside with a tap for the introduction of oxygen. The other end of this tube passes down into the bulb of the combustion tube. The top of the latter is provided with a collar, into which a cap can be fitted

and hermetically closed, whilst a narrow steel tube leads from the cap and is connected with the ordinary absorption bulbs. The tube is heated from the upper part downwards by means of a blowpipe. When the upper part of the tube becomes bright red the lower part is heated by means of a second blowpipe.

A weighed quantity of the substance is introduced, and the tube filled with cupric oxide, which is pressed down as much as possible. The cover is then fixed on and connected with the absorption bulbs, and the tube heated as described above. As soon as bubbles of gas cease to be evolved the tap of the side tube is opened, and a slow current of oxygen passed through for about fifteen minutes. In the case of readily combustible bodies the combustion is complete within an hour, whilst for less combustible bodies the time is slightly increased, but in every instance the results are stated to be much more exact than those obtained by other methods. The apparatus can also be used for the combustion of liquids and gases. In the case of volatile liquids a weighed quantity of the substance is placed in a tube provided with a tap at each end, one being connected with the side tube of the apparatus, whilst a current of oxygen, heated by passing through a red-hot tube, enters by the other. The tube is first heated, and when the cupric oxide becomes red-hot the mixture of liquid and hot oxygen is slowly introduced. A similar plan is adopted for the combustion of gases, but in this case the oxygen is used at the ordinary temperature. C. A. M.

INORGANIC ANALYSIS.

Mercury Assay. R. Biewend. (*Berg. u. Hüttenmänn. Zeit.*, 1902, lxi., 441; through *Chem. Zeit. Rep.*, 1902, 251.)—The author has modified Eschka's dry method of determining mercury as follows: The sample is finely ground, dried over sulphuric acid, and a quantity is taken which does not contain more than 0·15 gramme of mercury. This is covered with a layer of copper filings, 0·3 to 0·5 centimetre deep, in a porcelain crucible, and the whole is covered with magnesia, or kieselguhr and asbestos. The gold basins weigh 10 to 12 grammes each, and have a cavity 3·5 to 4 centimetres in diameter by 0·75 centimetre deep, with a rim 0·5 centimetre wide. The crucible is supported by means of a perforated piece of asbestos sheet, so that the edges of the gold basins are protected from the heat. The crucible is first heated gently for ten minutes with a spirit-lamp; then the gold basin is changed for another, and ignition is continued for ten minutes at a higher temperature, which makes the bottom of the crucible appear red. The cooling water in the basins is renewed during the operation. F. H. L.

Volumetric Estimation of Gold with Thiosulphate. F. Faktor. (*Casopis. pro prumysl chemicky*, 1902, vi., 183; through *Chem. Zeit. Rep.*, 1902, 200.)—If a neutral solution of gold chloride is treated with an excess of potassium iodide, the original green precipitate of gold iodide redissolves, yielding a brown liquid which contains AuI_4K. On adding to this slowly a dilute solution of thiosulphate, the double iodide loses two atoms of iodine, becoming AuI_2K. On this reaction the

author bases his process, using 4 grammes of potassium iodide, decinormal thiosulphate, and starch as indicator. F. H. L.

A Colorimetric Method of Determining Arsenious Acid. J. Mai (*Zeit. anal. Chem.*, 1902, xli., 362-365.)—The author's method is based on the conversion of the arsenic compounds into arsenious chloride, and of the latter into arsenic trisulphide. The determination is carried out in an apparatus similar to that employed by Wiborgh for the determination of hydrogen sulphide. In preparing standard deposits, the arsenic trioxide was cautiously heated with hydrochloric acid (specific gravity 1·19) in a large test-tube and the arsenious chloride slowly distilled over, whilst a current of dry carbon dioxide was simultaneously passed through the apparatus. The gases passed through a U-tube and then into a wide-mouthed tube, the open end of which was covered with moist cotton impregnated with zinc sulphide. The cotton cloth had been soaked in zinc sulphate solution and then subjected to the action of hydrogen sulphide. It was fixed to the mouth of the tube by means of a rubber ring, and the tube itself was immersed in water saturated with fresh hydrogen sulphide. In order to prevent the cloth being blocked, a few pinholes were made, which, however, did not allow any of the arsenic to pass through. The mirrors given by quantities of arsenic, ranging from 0·1 to 0·6 milligramme, showed marked differences between each other, but above 0·6 milligramme the increase in intensity was only perceptible after the addition of 0·2 milligramme. C. A. M.

The Quantitative Determination of Small Quantities of Arsenic. C. T. Mörner. (*Zeit. anal. Chem.*, 1902, xli., 397-413.)—The method is based upon the oxidation of arsenic trisulphide by means of alkaline permanganate,

$$5As_2S_3 + 28KMnO_4 + 27SO_3 = 5As_2O_5 + 14K_2SO_4 + 28MnSO_4,$$

according to which 1 c.c. of $\frac{N}{100}$ potassium permanganate solution is equivalent to 0·0536 milligramme of arsenic. In the titration the arsenic trisulphide is dissolved in alkali (0·5 per cent. potassium hydroxide solution) and treated with 25 c.c. $\frac{N}{100}$ permanganate solution. After shaking the flask, 5 c.c. of 5 per cent. sulphuric acid are introduced, the liquid heated until colourless, and titrated back with $\frac{N}{100}$ permanganate solution.

In applying this method to the determination of arsenic in fabrics, such as carpets, etc., the sample is distilled with concentrated hydrochloric acid, and the distillate received in dilute nitric acid and evaporated to dryness, or the distillate is collected in water, the arsenic precipitated with hydrogen sulphide, the precipitate dissolved in ammonium hydroxide, and the solution evaporated to dryness. In either case the residue will contain organic substances capable of oxidation. To eliminate these the dry residue is heated on the water-bath, and treated successively with 2 c.c. of 0·5 per cent. potassium hydroxide solution; then, after about one minute, with 2 c.c. of 5 per cent. permanganate solution and heated for three minutes; then with 2 c.c. of 5 per cent. sulphuric acid and heated for three minutes;

and, lastly, with 1 c.c. of 20 per cent. tartaric acid solution and heated until colourless. The liquid is now filtered into another small basin, the first basin being rinsed with 2 c.c. of water. The second basin is placed on the water-bath, and after about one minute 1 c.c. of 5 per cent. thio-acetic acid is introduced, and the basin heated for three minutes, and left to cool for about five minutes. The precipitated arsenic trisulphide is collected and washed twice with 5 c.c. of 0·5 per cent. sulphuric acid, and then three times with 2 c.c. of water. It is then washed by means of three successive portions of 2 c.c. each of 0·5 per cent. potassium hydroxide solution into a flask containing $\frac{N}{100}$ permanganate solution, and the arsenic determined as described above, with the addition that a correction of 0·3 c.c. is made for substances extracted from the filter-paper by the alkali.

The author gives a detailed account of the results of forty test experiments in which small quantities of arsenic (0·17 to 0·25 milligramme) were added to different fabrics, etc. The differences between the amounts taken and found varied from −0·03 to +0·04 milligramme. C. A. M.

Use of Sulphuric Acid as a Solvent for Minerals rich in Arsenic, Iron, and Lead. H. Nissenson and F. Crotogino. (*Chem. Zeit.*, 1902, xxvi., 847.)—The authors call attention to the great superiority of suphuric acid over nitric or hydrochloric acid for the dissolution of substances containing a large proportion of arsenic or lead. In the first place, conversion of the arsenic and antimony into their more highly oxidized state is avoided, so that the subsequent precipitation with sulphuretted hydrogen is easier to manage; and, in the second place, danger of losing arsenic by volatilization of arsenious chloride is prevented. The material, finely ground and dried at 100° C., is heated with three times its weight of strong sulphuric acid for thirty minutes to three hours—*i.e.*, till everything which is soluble has been attacked; the liquid is then cooled quickly, diluted with hot water (not cold), allowed to settle, and filtered. In presence of antimony the residue is extracted with ammonium tartrate, and the gangue is filtered off; the lead is precipitated with a further amount of sulphuric acid, while any antimony in the filtrate therefrom is added to the bulk solution obtained after treatment of the diluted sulphuric acid solution with sulphuretted hydrogen. In their original article the authors give full details as to the adaptation of their methods to various ores, such as copper and iron pyrites, arsenical pyrites, lead ores, particularly lead glance, and minerals containing zinc and lead. Zinc ores containing much lead or iron may be very conveniently analysed or arsenic and antimony by the same process. F. H. L.

Determination of Tin, and its Separation from Antimony. C. Ratner. (*Chem. Zeit.*, 1902, xxvi., 873.)—The author recommends with Rössing (ANALYST, 1902, xxvii., 99), Clark's method as being the only accurate one for separating tin from antimony; but the second precipitation of the antimony sulphide advocated by Rössing is not necessary, provided the original solution was not too concentrated—*i.e.*, did not contain more than 0·5 gramme of tin plus antimony per 600 or 700 c.c.

Both Clark's and Rössing's processes for the estimation of the tin in the

antimony filtrate are objectionable, and the following method is preferable: The sulphuretted hydrogen is driven out of the liquid, and a fragment of pure zinc, as compact as possible, is dropped into the beaker, which is heated over gauze without permitting its contents to boil for some twenty minutes till a qualitative test shows that all tin has been thrown out of solution. The metallic residue is then collected on a paper, whence it is rinsed back into a small beaker with about 15 c.c. of water. Here it is treated with 10 c.c. of nitric acid, the temperature being adjusted to cause smooth dissolution. When all the zinc has disappeared the volume of the liquid is made up to 40 or 50 c.c., the precipitate is boiled up, allowed to settle, washed by decantation, and finally thrown on a paper, dried, ignited, and weighed. As metastannic acid filters badly, some ammonium nitrate may be added to the solution. The zinc occasionally becomes covered with a glass-like crust, but this does not appear to happen until all the tin has been deposited; and if it be formed the analysis is not affected. Three examples are given in which the figures obtained by the present method agree well with those of Rössing's and Clark's processes.

F. H. L.

Detection of Cadmium and Zinc by Blowpipe Tests. R. Biewend. (*Bery. u. Hüttenmänn. Zeit.*, 1902, lxi., 413 and 425; through *Chem. Zeit. Rep.*, 1902, 251.)—When an ore containing less than 1 per cent. of cadmium is heated before the blowpipe the usual brown sublimate of cadmium oxide fails to appear. In certain circumstances, however, a dull black, soot-like ring is produced, blue or violet at its inner edge, and this ring develops before the zinc sublimate. Antimony, bismuth, a few of the rare metals, and especially lead, interfere; otherwise the test shows 0·002 gramme in 1 gramme of substance. It indicates cadmium in brass foil. When zinc ores or alloys are heated in a glass tube before the blowpipe, using dry potassium oxalate as a reducing agent if necessary, cadmium yields a silver-white mirror of metal and a brown sublimate of oxide, which appears gray while hot. Lead, bismuth, and tin give no sublimates, and antimony only if it exists as sulphide. Full details are given respecting this test in the original article. F. H. L.

Separation and Precipitation of Thorium. A. Kolb. (*J. prakt. Chem.*, 1902, lxvi., 59; through *Chem. Zeit. Rep.*, 1902, 214.)—In order to precipitate the hydroxide from a solution of pure thorium nitrate, the liquid is acidified with a little hydrochloric or nitric acid, neutralized as far as possible with ammonia, and raised to the boiling-point. The boiling liquid is then treated, drop by drop, with aniline, shaking vigorously until a turbidity appears. The vessel is next put aside in a warm place till the precipitate settles, and the latter is washed by decantation with water at 50° C. Commercial thorium sulphate should first be mixed with ammonia, the hydroxide dissolved in hydrochloric acid, the solution neutralized with ammonia, and further treated as above, any ferric oxide or ceric oxide being reduced with sulphurous acid or sulphuretted hydrogen before adding the aniline. A solution of the chlorides or nitrates is most suitable for the separation of thorium by this method. F. H. L.

Iodometric Valuation of the Peroxides of Barium, Sodium, etc. E. Rupp. (*Arch. Pharm.*, 1902, ccxl., 437; through *Chem. Zeit. Rep.*, 1902, 251.)—The peroxides of the alkalies and alkaline earth metals may be valued by treating them with potassium iodide in presence of a little hydrochloric acid, and titrating the liberated iodine with decinormal thiosulphate and starch. The following is the reaction which takes place: $M''O_2 + 4HCl + 2KI = M''Cl_2 + 2KCl + 2H_2O + I_2$. F. H. L.

The Detection of Bromine and Iodine in the Presence of Thiosulphates. A. F. Leuba. (*Ann. de Chim. anal.*, 1902, vii., 298, 299.)—The solution of the salt is heated to the boiling-point, and the thiosulphate precipitated by means of a slight excess of lead nitrate. The liquid is boiled for fifteen minutes and then filtered, and the filtrate tested for iodine by the addition of chlorine water and carbon bisulphide. The lead iodide formed in the precipitation of the thiosulphate is sufficiently soluble in boiling water to give the violet reaction in the filtrate. For the detection of bromine, it is preferable to add a little fluorescein to the liquid rendered alkaline with sodium hydroxide, when a bright red colour is obtained in the presence of bromides.

C. A. M.

The Volumetric Determination of Iodides in the Presence of Bromides and Chlorides. Thomas. (*Comptes Rendus*, May 20, 1902; *Ann. de Chim. anal.*, 1902, vii., 349, 350.) –When a solution of a thallic salt, such as the chloride, is mixed with an excess of potassium iodide, a greenish-black precipitate, consisting of a mixture of thallous iodide and iodine, is formed. If, however, the thallic salt is in excess, only free iodine is liberated; and on this fact is based the author's method, in which the iodine is expelled from the liquid by boiling, and the unreduced thallic salt determined by titration. For this purpose the solution is mixed with an excess of standard thiosulphate solution and of potassium iodide (free from iodate) and 1 c.c. of starch-water, and titrated with a standard solution of iodine.

In applying the method in the presence of bromides, the liquid must not be overheated, but the free iodine expelled by means of a current of air.

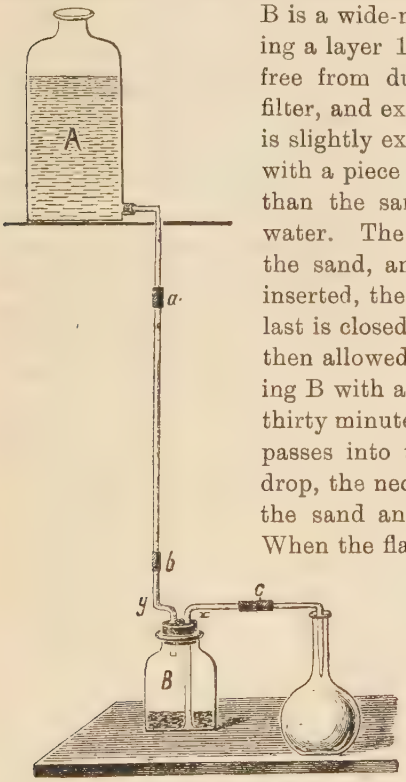
The precipitated thallous iodide can readily be converted into thallic chloride by treatment with hydrochloric acid and potassium chlorate. After removal of the chlorine by heating, the liquid is diluted, and gives a solution of thallic chloride which can be at once used again. There is practically no loss of thallium.

C. A. M.

The Titration of Free Alkali in the Presence of Nitrites. K. Arndt. (*Zeit. anal. Chem.*, 1902, xli., 359-362.)—If the solution of the nitrite be sufficiently cooled and a suitable indicator employed, the alkali can be titrated with standard acid. Thus, on cooling a solution of 1 gramme of sodium nitrite to 0° C., and titrating the liquid with $\frac{N}{10}$ sulphuric acid with methyl orange as indicator, there was hardly any perceptible odour of nitrogen peroxide, nor did the liberated nitrous acid turn the indicator red. Litmus as indicator gave still better results, although the change in

colour was not so sharp as in the absence of nitrites. If carbonates be present, it is necessary to precipitate them with barium chloride, and to titrate the filtrate with standard hydrochloric acid. In the case of aurin (rosolic acid) the change is sharper than in the case of litmus, but, since nitrous acid acts upon alcohol, it is necessary to employ an aqueous solution of the indicator. Here, too, carbonic acid must be removed before the titration. This method gave concordant results in determining the amount of free ammonia in a solution of ammonium nitrite. C. A. M.

Determination of Prussian Blue in Spent Oxide. R. Schwartz. (*Chem. Zeit.* 1902, xxvi., 874.)—The apparatus employed by the author for extracting spent gas-works oxide with sodium hydroxide and carbonate is shown in the annexed sketch.



B is a wide-necked bottle holding 100 to 150 c.c. and containing a layer 1·5 to 2 centimetres thick of coarse washed sand free from dust. The tube *x* passes right through the sand filter, and extends almost to the bottom of the bottle, where it is slightly expanded trumpet-fashion, having its orifice covered with a piece of brass or phosphor-bronze gauze finer in mesh than the sand particles. A is a pressure vessel filled with water. The weighed quantity of the sample is spread out on the sand, and the extracting fluid is added; the stopper is inserted, the rubber connections *a*, *b*, and *c* are made, and the last is closed with a screw clamp. Maceration in the cold is then allowed to proceed for one or two hours, or, by surrounding B with a water-bath, digestion in the hot is continued for thirty minutes. The clamp *c* is next opened so that the liquid passes into the 1-litre measuring flask on the right, drop by drop, the necessary pressure to determine percolation through the sand and gauze being given by the head of liquid in *y*. When the flask is full to the mark a few drops of liquid are collected in a test-tube, and examined for alkalinity and for ferrocyanogen. Generally the liquid is neutral and free from dissolved matter; if not, more water, or more sodium hydroxide, may be introduced through A and a second litre of extract collected. Finally, the ferrocyanides in the solution are determined as usual, preferably by gravimetric methods. The process gives results agreeing well with those of Knublauch's, and Moldenhauer and Leybold's methods; but it has the advantage of yielding a clear extract, and of showing when all soluble matter has been recovered. F. H. L.

The Behaviour of Selenious Acid in the Marsh Apparatus. J. Schindelmeiser. (*Zeit. für öffentl. Chem.*, 1902, viii. [16], 306-309.)—The addition of

0·25 gramme of selenious acid to a Marsh apparatus containing 10 grammes of pure zinc and about 100 c.c. of sulphuric acid (1 : 5) quickly caused the evolution of hydrogen to cease. A brown-red flocculent precipitate formed in the solution, and was found to consist of a mixture of selenium and zinc containing from 11 to 19 per cent. Zn. No selenium passed over into the combustion tube. When aluminium and soda were employed, selenious acid did not hinder the evolution of hydrogen. In the presence of arsenic (10 to 25 c.c. of a 0·05 per cent. solution of As_2O_3) no mirror was obtained until the selenious acid had been converted into the brown flaky condition. The arsenic then came over, none remaining with the zinc-selenium compound. W. P. S.

Use of Victor Meyer's Vapour Density Apparatus for Gas-volumetric Analysis. J. Mai and M. Silberberg. (*Chem. Zeit.*, 1902, xxvi., 875.)—This is a preliminary note suggesting an employment of V. Meyer's apparatus for the analysis of such substances as give off a gas on treatment with some liquid reagent. The latter is placed in the inner tube, and the solid is suspended in a bag of ignited asbestos above it. The apparatus is raised to some high temperature, and the level of the liquid in the burette is read off; then the solid is permitted to fall into the liquid, and when all gas has been evolved a second reading of the burette is taken. Experiments were first carried out with pure sodium carbonate decomposed in the cold with hydrochloric acid, correction being made for the solubility of the carbon dioxide in the water of the burette by means of Dietrich's tables. Afterwards the carbonate was decomposed with hot strong sulphuric acid to which 15 per cent. of sodium sulphate had been added with the view of rendering evolution of gas more gentle, the apparatus being maintained at a constant temperature by the use of boiling amyl acetate in the jacket. Oil is preferable to water in the measuring vessel, and mercury may be used with advantage. Some figures indicating the determination of carbon dioxide are recorded, which appear satisfactory. F. H. L.

A Gas-Volumetric Method of Alkalimetry. E. Riegler. (*Zeit. anal. Chem.*, 1902, xli., 413-419.)—The advantages claimed for this method are that it is rapid, very accurate, and obviates the use of all standard solutions. It is based upon the fact that hydrazine sulphate reduces the salts of iodic acid, thus :

$$(1)\ 5N_2H_4.H_2SO_4 + 4NaIO_3 = 2Na_2SO_4 + 3H_2SO_4 + 12H_2O + 4I + 5N_2.$$

The excess of hydrazine sulphate present then acts on the free iodine :

$$(2)\ N_2H_4.H_2SO_4 + 4I + 2H_2O = H_2SO_4 + 2H_2O + 4HI + N_2.$$

Hence the decomposition of an iodate by an excess of hydrazine sulphate can be represented by the equation,

$$(3)\ 6N_2H_4.H_2SO_4 + 4NaIO_3 + = 2Na_2SO_4 + 4H_2SO_4 + 4HI + 12H_2O + 6N_2;$$

and, according to this, 1 milligramme of nitrogen corresponds with 4·175 milligrammes of iodic acid, or 1 c.c. of nitrogen of 0° C. and 760 millimetres' pressure is equivalent to 5·2216 milligrammes of iodic acid. If, then, the equivalent quantity of a given base combining with iodic acid be known, its quantity can be calculated

from the amount of nitrogen. This weight, x, can be found by multiplying the volume of nitrogen at 0° C. and 760 millimetres pressure by the factor 0·0297, and multiplying the product by the equivalent of the base in question.

In making a determination the base is dissolved in 20 to 30 c.c. of water. After the addition of 2 to 3 drops of phenolphthaleïn solution a 2 per cent. solution of iodic acid is introduced drop by drop with continual shaking until the liquid becomes colourless. The solution is then placed in the exterior vessel of a Knop-Wagner nitrometer, whilst about 0·5 gramme of hydrazine sulphate is placed in the inner vessel, and the nitrogen liberated and measured in the usual manner. It is essential to shake the nitrometer flask during the evolution of the gas at intervals for about thirty seconds at a time until its contents become colourless. C. A. M.

The Determination of the Oxygen Absorption of Natural Waters. L. W. Winkler. (*Zeit. anal. Chem.*, 1902, xli., 419-426.)—The loss of oxygen on boiling 100 c.c. of acid $\frac{1}{100}$ N-permanganate solution was found by the author to be equivalent to 0·125 c.c., whilst in the case of an alkaline solution the average loss was 0·175 c.c. In the author's opinion, an alkaline solution is preferable, as the organic substances are more completely oxidized, and chlorides have a less disturbing influence. He has also made experiments to determine under what conditions a standard solution of oxalic acid will keep best, and finds that that acidified with sulphuric acid is the most satisfactory. Thus, the following comparative results were obtained, the initial values being taken as 100 :

	$\frac{1}{100}$ N-Oxalic Acid Solution.	$\frac{1}{100}$ N-Oxalic Acid Solution Neutralized.	$\frac{1}{100}$ N-Oxalic Acid Solution Acidified.	$\frac{1}{100}$ N-Oxalic Acid Solution rendered Alkaline.
Initial values	100·00	100·00	100·00	100·00
After 35 days	99·47	96·21	99·94	99·49
,, 61 ,, ...	99·24	93·92	99·89	98·87
,, 90 ,, ...	98·75	92·52	99·74	98·18
,, 183 ,, ...	98·34	87·87	99·69	96·07

The following method of determining the oxygen absorption is recommended: 100 c.c. of the water are kept boiling for ten minutes with 10 c.c. of $\frac{1}{100}$ N-alkaline permanganate, prepared with the usual precautions and standardized on $\frac{1}{100}$ N-oxalic acid solution. The liquid is then treated with 10 c.c. of dilute sulphuric acid (1 : 3) and 10 c.c. of $\frac{1}{100}$ N-oxalic acid solution, and, after it becomes completely colourless, the alkaline permanganate solution is introduced, drop by drop, from a burette until a faint pink colour remains. A correction of 0·3 c.c. is made, and the oxygen absorption expressed in terms of c.c. of $\frac{1}{100}$ N-permanganate solution reduced by 100 c.c. of the water. C. A. M.

APPARATUS.

Platinum Basin with Chimney and Draught-holes. **A. Hebebrand.** (*Zeit. für Untersuch. der Nahr. und Genussmittel*, 1902, v., 719-721.)—The apparatus consists of a platinum basin having a number of circular holes around and just below its edge. The basin is covered with an aluminium lid, from the centre of which a chimney rises. The latter is about 11 centimetres high and 1·8 centimetres in diameter. The top of the chimney is closed, the opening being at the side, so that no dust, etc., may fall into the basin. Substances which burn with difficulty, such as meat, bread, and sugar, are completely incinerated in about one-half the time usually required, and the amount of ash agrees closely with that obtained by igniting in an open basin. W. P. S.

Apparatus for Cold and Hot Filtrations. **P. N. Raikow.** (*Chem. Zeit.*, 1902, xxvi., 732.)—In the annexed sketches are shown jackets for surrounding funnels with either freezing mixtures or steam, which have the advantage over other devices that not only the sides, but also the top of the liquid being filtered is directly exposed to the desired temperature conditions. In the cold funnel (Fig. 1) the

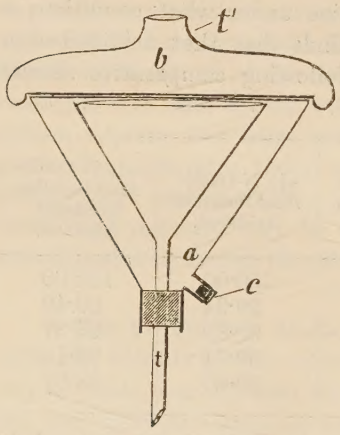


FIG. 1.

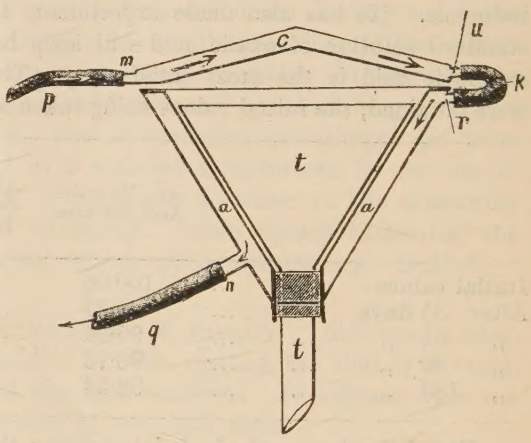
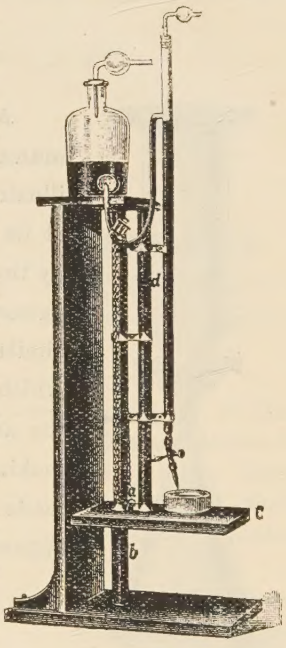


FIG. 2.

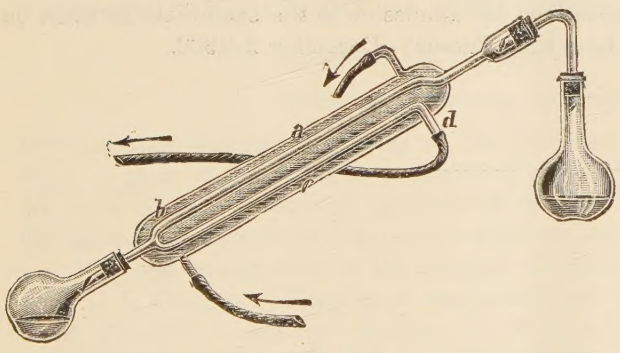
vessel *b* is a hollow dish with depending flange fitting round the jacket, and is filled with ice or freezing mixture. The inner funnel should be fixed as high as possible in the jacket, and the annulus filled completely, so that air-space may be reduced to a minimum. In the hot apparatus (Fig. 2) *c* is a coned cover connected at *p* with the steam-supply, and joined at *u* by means of the rubber tube *k* with the inlet of the lower jacket. If preferred, *k* may be done away with by making *u* and *r* vertical so as to form a telescopic joint. F. H. L.

Automatic Apparatus for Titrations. W. Schmidt. (*Chem. Zeit.*, 1902, xxvi., 734.)—This is a burette stand which automatically sets the burette at its zero-point, and is much simpler than most other patterns, avoiding the usual inconvenient rubber ball. The burette itself is clamped on to the rod *d*, which is rigidly connected with the little table *c*; *c* and *d* together slide up and down the rod *b* over a distance of about 14 centimetres. The chain shown in the diagram is fastened at one end to *c*, passes over a pulley at the top of *b*, and, when the table is at its highest position, is hooked over a pin *a* on the table on the further side. When not in use *c* is allowed to rest on the base of the main stand, in which position the zero-point of the burette is 2 centimetres below the lowest position of the liquid in the store bottle, and the reagent flows into the burette to fill it. When the small table is raised the zero-point is about 2 centimetres above the highest position of the liquid in the store vessel, and the reagent runs back through the curved rubber tube till the O-point is set correctly. The burette cannot overflow, as it is some 12 centimetres longer than the zero-spot. The elevated position of the small table is specially convenient during titration, since it renders the pinchcock or stopcock more accessible than usual. The apparatus is made by J. Brüncker and Co., of Ilmenau.



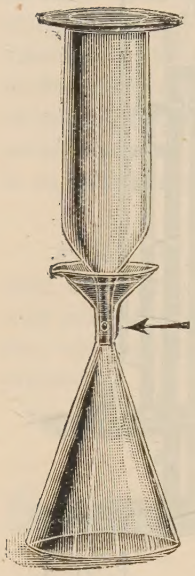
F. H. L.

Condenser for Volatile or Noxious Liquids. H. Goeckel. (*Chem. Zeit.*, 1902, xxvi., No. 55.)—This is an apparatus of the Liebig pattern, in which the inner tube is forked at the outlet end, one branch passing through a cork to the receiving flask, and the other returning backwards to the opposite extremity, where it is bent and passed through the outer wall. By this arrangement the condensing surface for a given length of water-jacket is doubled; while the tube *d* may either be connected to a second condenser when extremely volatile liquids are being distilled, or it may be coupled to a pump for distillations under diminished pressure. If the vapours are unpleasant or poisonous, the rubber tube fastened to *d* can be led into the draught cupboard. The tube *a* is shown as lying vertically over *e* for convenience of illustration, but actually they are twisted so as to



be in a horizontal plane. The apparatus is protected as a "Gebrauchsmuster," and may be obtained from Sauer and Goeckel, 49, Wilhelmstrasse, Berlin, W.

F. H. L.



A Modified Wiborgh Flask. H. Goeckel and J. Wolfmann. (*Stahl und Eisen*, 1902, No. 12.)—As shown by the illustration, the Erlenmeyer flask in this apparatus is expanded at its neck so as to form a funnel, while at the spot indicated by the arrow it is provided with a vertical channel. The lower extremity of the upper vessel is also provided either with a similar and opposite channel, or with a hole in its neck, through which liquid can be introduced into the flask. This device has the advantage of doing away with any glass stop-cock, and of making the apparatus less liable to injury. The joint may be made perfectly tight by pouring water into the funnel. The apparatus may be obtained from Sauer and Goeckel, Berlin.

F. H. L.

INSTITUTE OF CHEMISTRY.

Examinations of the Institute will be held in London during January, 1903. The Intermediate Examination will commence on January 6. Examinations on all branches of the Final, excepting Biological Chemistry, will commence either on January 6 or January 13. Applications for admission to the examinations must be forwarded to the Registrar not later than Tuesday, December 2, 1902.